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**Japanese Patent Application JP 2002 - 129483 A**

**Copolyester Wallpaper**

**Your Ref: 102203 - 15**

**For: Eastman Chemical Company**

9109 Eagle Hills Dr . Las Vegas NV 89134 . ph: 866-722-7990 (toll-free) . fax: 702-973-6009 . email: sales@tls-  
translations.com

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(71) Applicant: 000000550  
Okamoto Industries, Inc.  
27-12, Hongo 3 chome, Bunkyo-ku, Tokyo  
  
(72) Inventor: Yasuhiro TANAKA  
c/o Okamoto Industries, Inc.  
Shizuoka Branch, 1, Kobe, Yoshida-cho,  
Yohara-gun, Shizuoka-ken

(72) Inventor: Akira NAGATA  
c/o Okamoto Industries, Inc.  
Shizuoka Branch, 1, Kobe, Yoshida-cho,  
Yohara-gun, Shizuoka-ken  
  
(72) Inventor: Masao SASAKI  
c/o Okamoto Industries, Inc.  
Shizuoka Branch, 1, Kobe, Yoshida-cho,  
Yohara-gun, Shizuoka-ken  
  
(74) Agent: 100089406  
Hiroshi Tanaka, Patent Attorney  
(and two others)

(Continued on last page)

(54) [Title of the Invention]

Copolyester Wallpaper

(57) [Summary]

[Object] To provide wallpaper that possesses improved flame retardance, calenderability, foamability, dent resistance, and surface smudging properties.

[Means of Achievement] A polyester wallpaper, characterized in that the polymer that constitutes the resin layer is a copolyester, and the resin layer comprises 100 parts by weight of

the aforementioned polymer and 30 to 500 parts by weight with regard to this polymer of an inorganic compound that imparts flame retardance; in particular, a polyester wallpaper characterized in that 1 to 50 parts by weight of a thermoplastic elastomer is admixed per 100 parts by weight of the copolyester that constitutes the aforementioned resin layer.

**[Claims]**

**[Claim 1]** A polyester wallpaper, characterized in that the polymer that constitutes the resin layer is a copolyester, and said resin layer comprises 100 parts by weight of said polymer and 30 to 500 parts by weight with regard to the polymer of an inorganic compound that imparts flame retardance.

**[Claim 2]** The polyester wallpaper according to Claim 1, characterized in that the polymer that constitutes the resin layer is compounded with 1 to 50 parts by weight of a thermoplastic elastomer per 100 parts by weight of the copolyester.

**[Claim 3]** The polyester wallpaper according to Claim 1 or 2, characterized in that the copolyester has a glass transition point of 50°C or lower, and that the resin layer contains essentially no plasticizer.

**[Claim 4]** The wallpaper according to Claim 1, 2, or 3, wherein the inorganic compound that imparts flame retardance is selected from calcium carbonate, aluminum hydroxide, or magnesium hydroxide, alone or as a mixture.

**[Detailed Description of the Invention]**

**[0001]**

**[Technological Field of the Invention]** The present invention relates to wallpaper having excellent calenderability and the flame retardance required of wallpaper, as a result of a specific copolyester having been compounded with an inorganic substance that imparts flame retardance.

**[0002]**

**[Prior Art]** Polyvinyl chloride wallpapers comprising a soft polyvinyl chloride foam layer and a paper layer that serves as a substrate are currently in wide used. Polyvinyl chloride wallpapers have properties such as good flame retardance, which is derived from the resin, and good calenderability, which accordingly make them ideally used as wallpaper. However, concerns have been raised in recent years about, among other things, the production of chlorine-based

gases during the evaporation and combustion of the plasticizer that is used for softening purposes, and concerted efforts have been made to develop a wallpaper that can be used as a substitute. Wallpaper in which polyolefin resin is employed has been developed as such a material. However, polyolefin resin is essentially highly combustible, poorly suited to calendering, and has poor foamability; therefore, the resin layer must be thickened in order for the finished product to appear to have depth, which increases the amount of heat generated on combustion. Accordingly, such wallpaper has not been extensively used.

[0003] Polyethylene terephthalate, which is a common polyester resin, is less combustible than polyolefin [resin], but its poor calenderability and foamability render it inappropriate for use in wallpaper. Japanese Patent Application (Tokugan) No. 2000-123512 presents a wallpaper made from a copolyester, but dents are made when a roll of the product is spread out, which is not a problem with ordinary polyvinyl chloride wallpaper. Moreover, a plasticizer is used in order to soften the resin layer, as with ordinary polyvinyl chloride wallpapers, but plasticizers are preferably not used in order to avoid contaminating the air inside the room. In addition, dents remain in the wallpaper in Japanese Patent Application (Tokugan) No. 2000-123512 once a roll has been spread out immediately after being processed. While these problems can be avoided with certain storage methods, the wallpaper cannot be handled like conventional polyvinyl chloride wallpapers, and thus proves inconvenient.

[0004]

**[Problems That the Invention Is Intended to Solve]** It is accordingly an object of the present invention to provide a wallpaper having good flame retardance, calenderability, and foamability, and that is produced from a copolyester. A further object is to provide a wallpaper that essentially does not contain a plasticizer, and that is not susceptible to roll denting.

[0005]

**[Means Used to Solve the Above-Mentioned Problems]** The present invention is a polyester wallpaper characterized in that 30 to 500 parts by weight of an inorganic compound that imparts flame retardance is added to 100 parts by weight of a copolyester as the resin layer. Moreover, the present invention is a polyester wallpaper that remedies the problem of roll dents by means of admixing a thermoplastic elastomer to the copolyester, which is the polymer that constitutes the

resin layer. Further, the present invention is a wallpaper in which a copolyester with a glass transition point of 50°C or lower is used, thereby essentially obviating the addition of a plasticizer.

[0006]

**[Embodiments of the Invention]** The present invention will now be described in further detail.

#### Copolyester

As referred to herein, the term "copolyester" refers to a copolyester of a polycarboxylic acid and/or a polyhydric alcohol, obtained through the random copolymerization of two or more polycarboxylic acids or polyhydric alcohols. The copolyester therefore has a low crystallinity. A copolyester having a T<sub>m</sub> of 200°C or lower according to DSC is suitable for calendering, and an amorphous polyester that does not have a T<sub>m</sub> according to DSC is preferably suited to calendering.

[0007]

Adipic acid, glutaric acid, succinic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid, and other aliphatic acids are examples of polycarboxylic acids that are used for in the manufacture of such polyesters. 1,4-Cyclohexane dicarboxylic acid and cyclohexane diacetic acid are examples of alicyclic acids that can be used. Terephthalic acid, orthophthalic acid, isophthalic acid, 2,6-naphthalene dicarboxylic acid, 2,6-naphthalene dimethylene carboxylic acid, paraphenylene dicarboxylic acid, trivalent carboxylic acids such as trimellitic acid, and tetravalent carboxylic acids such as pyromellitic acid are examples of aromatic acids that can be used. However, the maximum amount of a carboxylic acid that has three or more carboxyl groups is 0.5 mol%. It is understood that acid anhydrides, esters, and acid chlorides corresponding to these acids are also included. Monomers among those above that have a cyclic structure and tend not to rotate, such as 1,4-cyclohexanedicarboxylic acid, are undesirable because their glass transition point will increase, thereby preventing their use in large amounts. Adipic acid and the like, which have methylene chains that tend to bend, are preferred because their glass transition point will decrease, thereby providing flexibility.

[0008]

Examples of aliphatic polyhydric alcohols include ethylene glycol, 1,2-propylene glycol, 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, diethylene glycol, triethylene

glycol, polyethylene glycol (up to a degree of polymerization of about 5), polytetramethylene glycol, 2,2-dimethyl trimethylene glycol, and hexamethylene glycol. Other examples include trihydric and tetrahydric alcohols, such as trimethylolpropane and pentaerythritol. Examples of alicyclic variants include 1,4-cyclohexanedimethanol, and examples of aromatic variants include bisphenol A. It is desirable for there to be a maximum amount of approximately 0.5 mol% alcohols that have three or more hydroxyl radicals in terms of the moldability of the resulting polyester. Monomers among those above that have a cyclic structure and tend not to rotate, such as 1,4-cyclohexane dimethanol, are undesirable because the glass transition point will increase, thereby preventing large amounts from being used. 1,6-Hexanediol and the like, which has a methylene chains that tend to bend, are preferred because their glass transition point will decrease, thereby providing flexibility.

[0009]

Copolyesters with a glass transition point of 20°C or lower are particularly preferred because their flexibility obviates the use of a plasticizer, and because roll denting is relatively infrequent. DC427, which is manufactured by Mitsubishi Rayon Co., Ltd. (glass transition point: 3 to 5°C), is an example of a copolyester with a glass transition point of 50°C or lower. PETG6763, manufactured by Eastman Chemical Co., Ltd. (glass transition point: 81°C), which comprises approximately 70% ethylene glycol units and approximately 30% 1,4-cyclohexanedimethanol units as the alcohol is an example of a copolyester whose glass transition point exceeds 50°C.

[0010]

In the present invention, 30 to 500 parts by weight of an inorganic compound is added to 100 parts by weight of copolyester. The inorganic compound is used in the form of a fine powder. Metal compounds having properties appropriate for wallpaper; i.e., having a good capacity for being admixed and retaining their foamability when admixed even in large amounts, are preferably used as the inorganic compound. Examples of metal compounds include oxides, hydroxides, carbonates, sulfates (and sulfites), silicates, borates and other compounds of metals such as aluminum, magnesium, calcium, zinc, titanium, iron, tin, and antimony. Calcium carbonate, aluminum hydroxide, and magnesium hydroxide are particularly preferred. If too little is added, the flame retardance will be insufficient, while if too much is added, calenderability will deteriorate. 50 to 100 parts by weight is a particularly preferred amount.

**[0011]**

A (meth)acrylic acid polymer can also be admixed in the present invention in order to improve foaming properties, calenderability, and other attributes. Specific examples include methyl (meth)acrylate homopolymers, as well as copolymers in which methyl (meth)acrylate accounts for 50 to 95 wt% of the polymeric components and in which examples of the copolymer component including methacrylic acid esters of alcohols with 2 to 18 carbons, acrylic acid esters of alcohols with 1 to 18 carbons, styrene,  $\alpha$ -methyl styrene, and other aromatic vinyls, as well as acrylonitrile, methacrylonitrile, maleic acid, and itaconic acid. These copolymer components can be used alone or in combinations of two or more. Moreover, it is particularly preferred for the weight-average molecular weight of these (meth)acrylic acid polymers to be within a range of 500,000 to 5,000,000. Specific product names include Metablen P-501, 530, 531, 550, and 551, which are marketed by Mitsubishi Rayon Co., Ltd.

**[0012]**

A lubricant may also be used in the present invention in order to improve calenderability. Examples include conventionally known phosphoric acid esters and fatty acid metal salts. Mixtures of monofatty acid phosphoric acid esters and di-fatty acid phosphoric acid ester are particularly good phosphoric acid esters. Examining the properties of a lubricant mixture comprising the lubricant used in the present invention has confirmed that the effect of the lubricant can be enhanced with the aid of low-density oxidized polyethylene waxes and high-density oxidized (partially oxidized polyethylene with an acid value of 1 to 40 mg KOH/g and an average molecular weight of 10,000 or less). The amount of polyethylene wax to be admixed is preferably 0.01 to 5.0 parts by weight per 100 parts by weight of copolyester. Examples include AX-518I made by Daikyo Kasei Co., Ltd. (a mixture of monostearyl phosphoric acid ester and distearyl phosphoric acid ester in a ratio of 6:4 and a mixture of low-density oxidized and high-density oxidized polyethylene wax (partially oxidized polyethylene with an acid value of 1 to 40 mg KOH/g and an average molecular weight of 10,000 or less)).

**[0013]**

A plasticizer may also be used in the present invention in order to enhance flexibility. Although the problem of evaporation can be virtually eliminated as long as the molecular weight is high, the problems of migration and contamination remain; therefore, a plasticizer is preferably not used. The plasticizer preferably has good compatibility with the polymer, and therefore the SP

(solubility parameter), which is a measure of this compatibility to a certain degree, should be 8.7 or higher, and preferably 9.0 or higher. Moreover, a plasticizer with a structure similar to that of the components that constitute the polyester is preferred from a chemical structure perspective. Plasticizers that are used with polyvinyl chloride, including phthalic acid esters, aliphatic dibasic acid esters, trimellitic acid esters, epoxidated oils, and adipic acid polyesters may be used as the plasticizer. However, compounds having a polyalkylene oxide structure with ethylene oxide ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ) units and/or propylene oxide ( $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-$ ) units, which have not been used as polyester resin plasticizers in the past, are compatible with copolyesters and are very effective as a plasticizer. Ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, and the like, as well as ester or ether compounds thereof are examples of preferred plasticizers that have ethylene oxide ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ) units. Similarly, propylene glycol, dipropylene glycol, tripropylene glycol, and the like as well as esters and ethers thereof are examples of plasticizers that have propylene oxide ( $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-$ ) units. In addition, polyalkylene glycol compounds comprising ethylene oxide ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ) units and propylene oxide ( $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-$ ) units, as well as comprising blocks of polyethylene oxide and polypropylene oxide, are obviously useful as plasticizers that constitute the polyester composition of the present invention. Ethylene oxide adducts of poly(propylene oxide) glycol and copolymers of ethylene oxide and propylene oxide are examples of substances that have both of the above-mentioned structures. Examples of ether compounds include alkyl phenol ethylene oxide  $n$ -mole adducts, and higher alcohol ethylene oxide  $n$ -mole adducts, and examples of ester compounds include aliphatic ethylene oxide  $n$ -mole adducts, and ethylene oxide  $n$ -mole adducts of aliphatic dibasic acid esters. Examples of other compounds having the above-mentioned units include ethylene oxide  $n$ -mole adducts of higher fatty acid amines, ethylene oxide  $n$ -mole adducts of fatty acid amines, and ethylene oxide  $n$ -mole adducts of bisphenol A. RS-1000 (polyether ester) manufactured by Asahi Denka Co., Ltd., is a specific example. Fatty acid glycerin esters also are compatible with copolyesters and are very effective as plasticizers. Examples of fatty acids include formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, tetracosanoic acid, undecanoic acid, oleic acid, elaidic acid, petroselinic acid, erucic acid, linolic acid, and linoleic acid. Diacetylated monofatty acid glyceride is especially preferred from among monoglycerides, diglycerides, triglycerides and acetylated glycerides of

singular fatty acids or a plurality thereof. PL-012G (glycerin diacetomonolaurate) manufactured by Riken Vitamin Co., Ltd. is a specific example.

**[0014]**

It is preferred that 1 to 50 parts by weight of a thermoplastic elastomer is added per 100 parts by weight of the copolyester in the present invention to avoid roll dents. Examples of thermoplastic elastomers include styrene, polyolefin, polyurethane, polyamide, polyvinyl chloride, polyester, and fluorine rubber systems. Of these, styrene systems are preferred because of their good flexibility and compatibility with copolyesters, and their performance with regard to roll dents and flexibility is especially good when 1 to 20 parts by weight of SIS (polystyrene-polyisoprene-polystyrene thermoplastic elastomer) is added. D-1117 (SIS) manufactured by Shell Japan Co., Ltd., is a specific example thereof.

**[0015]**

Foaming is preferably induced in accordance with the present invention. A chemical foaming agent, such as ADCA (azodicarbonamide), OBSH (P,P'-oxybis(benzenesulfonyl hydrazide)), TSH (para-toluenesulfonyl hydrazide), DPT (dinitropentamethylene tetramine), or a mixed blend of these foaming agents, is preferably used as a foaming agent for the resin composition that forms the foaming copolyester layer. An example of an ADCA foaming agent is #3170 (Otsuka Kagaku Co., Ltd.). The above-mentioned foaming agents may be combined with the above-mentioned copolyester resin composition to produce a foaming decorative sheet having good foaming properties. Adding 0.5 to 5 parts by weight of a urea, organic acid, metal salt or other foaming agent system (kicker); e.g., zinc oxide or zinc stearate, will reduce the temperature at which decomposition of the foaming agent starts, because such an addition affects the softening temperature of the copolyester that will be used, which will thereby improve foamability. A foaming rate of 2 to 20 times is preferable, and 5 to 20 times is ideal. It is important for the wallpaper to be as light as possible in order for the flame retardance property as represented by the temperature-time area (corresponding to  $td\theta$ ), which exceeds the standard temperature curve specified in JIS A1321 for wallpaper, to be satisfactory. Therefore, a foam structure is beneficial for making the wallpaper lighter while making it appear as having the necessary thickness, and consequently the materials used to make the wallpaper must have good foamability, and a foaming rate of at least 2 times, with a foaming rate of at least 5 times being necessary to produce the appearance of depth. However, full value as a commercialized product cannot

currently be realized if the foaming rate is 20 times or more, as rough cells will be very prominent.

**[0016]**

Calendering can be used to work the wallpaper of the present invention, and film with a thickness of 0.1 to 1.0 mm can be manufactured. The appropriate temperature range for calendering is 100 to 220°C, and is preferably 120 to 200°C. Wallpaper having a substrate layer can be manufactured by means of subjecting the paper that is used for the wallpaper substrate to a lamination process involving the application of heat and pressure. Furthermore, ornamenting, delustering, or other treatments may be performed thereon. For example, a method that may be adopted as one decorative printing means (pattern printing) involves printing with printing ink using an acrylic resin and/or urethane resin vehicle on the engraving roll of a gravure printing press, then drying the resulting product in a drying furnace. A method whereby a luster-adjusting agent is applied by means of the the same printing processes as described above may also be used for delustering or other surface treatments. The above-mentioned acrylic resin and/or urethane resin treatment agent may also be used as the treatment agent vehicle. The wallpaper of the present invention is also preferred in terms of its good compatibility with ink and treatment agents. Furthermore, the wallpaper of the present invention also has good embossing transfer properties.

**[0017]**

**[Working Examples]** Working Examples 1 through 9 and Comparative Example 1

The polyester resin compositions for calender molding cited in Table 1 were prepared. Calenderability was evaluated with test rolls. The roll temperature was 150°C, the rotation rate was 30/25 (rotations/minute), and the roll gap was (mm) [*sic*]. An evaluation of "A" was recorded when there were no problems with the bank state ("C" was recorded if the texture was rough) or with the state of the sheet selvages ("C" was recorded if indentations were present), while an evaluation of "B" was recorded if there were slight problems. Calendering was performed to manufacture 0.12 mm-thick sheets having the compositions shown in Table 1, the sheets were laminated together with common 65 g/m<sup>2</sup> wallpaper, normal pattern printing was performed during the printing step, and common foaming and embossing processes were performed, resulting in a wallpaper product that was 0.8 mm thick. The wallpapers were rolled

in 50-m lengths, and three rolls were stacked on top of one another. The rolls were observed macroscopically for dents, with "C" being recorded when denting was clearly defined, "B" when the denting was visible on close inspection, and "A" when no denting was present. Foamability was evaluated macroscopically based on the surface state of the product, with "C" being recorded if the surface was rough or foaming was inadequate, "B" when some surface roughness was evident or foaming was only slightly inadequate, and "A" when the foamability was good. Flame retardance was tested in accordance with JIS A1321-1975, with wallpaper that passed flame retardance grade 2 being recorded as "A", and wallpaper that did not pass flame retardance grade 2 being recorded as "B".

[0018]

[Table 1]

		WE1	WE2	WE3	WE4	WE5	WE6	WE7	WE8	WE9	CE1
Copolyester	DC427 (Mitsubishi Rayon)	100	100	100	100	100	100				100
Copolyester	PET-G6763 (Eastman Chemical)							100	100	100	
Foaming agent	#3170 (Otsuka Kagaku)	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8
Plasticizer	RS-1000 (Asahi Denka)							22	22		
Plasticizer	PL-012G (Riken Vitamin)									22	
Thermoplastic elastomer	D-1117 (Shell Japan)		3	10	3	3	1	3	1	3	
(Meth)acrylic acid polymer	Metablen P-530 (Mitsubishi Rayon)	1	1	1	1	1	1	1	1	1	1
Phosphoric acid ester lubricant and polyethylene wax	AX-5181 (Daikyo Kasei)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Lubricant	Zinc stearate	1	1	1	1	1	1	1	1	1	1
Inorganic compound	Calcium carbonate	60	60	60	300		60	60	60	60	10
Inorganic compound	Aluminum hydroxide					20					
Inorganic compound	Magnesium hydroxide					20					
Colorant	Rutile-type titanium oxide	8	8	8	8	8	8	8	8	8	8
Calenderability		A	A	A	B	A	A	A	A	A	A
Foamability		A	A	A	B	A	A	A	A	A	A
Flame retardance		A	A	A	A	A	A	A	A	A	C
Denting		B	A	A	A	A	A	A	B	A	A

["WE" = working example; "CE" = comparative example]

[0019]

[Effect of the Invention] As has been described in the foregoing, the present invention offers good calenderability and improved flame retardance, foamability, and surface smudging properties as wallpaper, while having the exceptional effect of being able to provide a wallpaper that is resistant to denting.

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